ORIGINAL ARTICLE

Novel phenylethynyl-terminated PMDA-type polyimides based on KAPTON backbone structures derived from 2-phenyl-4,4'-diaminodiphenyl ether

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Novel phenylethynyl-terminated addition-type imide oligomers (degree of polymerization, $n=4$) derived from 1,2,4,5-benzenetetracarboxylic dianhydride, 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA), which has an asymmetric and nonplanar structure, and 9,9-bis(4-aminophenoxy)fluorene were synthesized for use as the matrix resin of fiber-reinforced composites with high heat resistance. The uncured imide oligomers showed good solubility (>30 wt%) in aprotic solvents such as *N*-methyl-2-pyrrolidone and very low minimum melt viscosity. These excellent properties were achieved using steric hindrance of the pendant phenyl group of p-ODA in a solution or a melted state to prevent the intramolecular/intermolecular interactions of imide oligomer chains. The imide oligomers were converted to crosslinked structures after curing at 370 °C for 1 h. Thermal and rheological properties of the cured resins were characterized by differential scanning calorimetry, thermogravimetric analysis and dynamic rheometry. The glass transition temperature and elongation-at-break of the cured imide resin were found to be almost >350 °C and $>15\%$, respectively. These excellent properties of pyromellitic dianhydride-based and p-ODA-based addition-type aromatic polyimides are promising for applications in highly heat-resistant composites.

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INTRODUCTION

Wholly aromatic polyimides (PIs) such as KAPTON and APICAL (DuPont and Kaneka, respectively) and UPILEX-R (Ube Industries) are well known for their high glass transition temperature (T_g), outstanding environmental stability, high dimensional stability and a low coefficient of thermal expansion.^{1–3} These properties are attributed not only to their rigid (planar and symmetric pyromellitimide or biphenylimide) structures, but also to the formation of highly ordered structures beyond T_g . Accordingly, these aromatic PIs do not display high molecular mobility at temperatures higher than T_g , indicating that the processing conditions for molding must be extremely severe.

Polyimide/carbon fiber composites are promising for use as lightweight materials in place of alloys of aluminum, steel and titanium in aerospace components used in high temperature applications. Over the last 30 years, many addition-type PIs have been reported for use as advanced composite materials in aerospace applications. For example, PMR-15, prepared from the reaction of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 4,4'-methylenedianiline with a nadic acid derivative for the reactive end cap, is a composite resin used at temperatures as high as 300 °C. However, the cured resin is brittle because of its high crosslink density and is difficult to mold.⁴ As a

result, PMR-15 composites exhibit poor impact resistance or compressive strength after impact. As another example, PETI-5 was prepared from the reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,4'-oxydianiline, 1,3-bis(3-aminophenoxy)benzene with 4-phenylethynyl phthalic anhydride (PEPA) for the reactive end cap at a calculated molecular weight of 5000 g mol⁻¹ in 1994.^{5–7} The cured PI exhibits a moderate T_g of 270 °C and more than 30% elongation-at-break (ϵ_b) for a film at room temperature. Because the formation of the converted cured resin was mainly a result of chain extension of the imide oligomers, arising from the thermo-additional polymerization of PEPA,^{8–10} the cured PETI-5 shows very similar properties to that of a thermoplastic and not a thermoset. Furthermore, it was noted that the phenylethynyl end cap offers distinct advantages such as a large processing window and good thermo-oxidative stability when cured compared with other reactive end caps such as nadic acid derivatives and maleic acid. In general, to obtain good processability and high fracture toughness, heat-resistant resins must have properties resembling those of PETI-5. Therefore, if these resins are to achieve good processability, the oligomer must possess a low melt viscosity. As a result, the imide oligomer between the end caps must maintain thermoplasticity through a flexible structure and a low T_g . However, the cured resin must exhibit a

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high T_g , which might appear to be in contradiction with the processability for heat-resistant polymeric matrix resins.^{11,12}

Yokota and co-workers^{13–15} previously reported ground-breaking thermoplastic PIs derived from asymmetric and nonplanar 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) that exhibited high T_g and a large drop of the storage modulus (E') above T_g as observed in dynamic mechanical analysis (DMA) measurements. These phenomena were found to be quite different from the symmetric PI derived from 3,3',4,4'-biphenyltetracarboxylic anhydride (s-BPDA). The results show that the irregular geometry of a-BPDA restricted the free rotation in the biphenyl linkage, resulting in the nonplanar structure of the biphenyl linkage and causing a decrease in the intensity of the intermolecular interaction that forms a nonplanar structure of PI chains.¹⁶ In addition, a large rotational unit in a PI chain increases T_g . On the basis of the thermal and rheological behavior of a-BPDA-based PIs, Yokota and co-workers¹⁷ have also designed a-BPDA-based phenylethynyl-terminated, addition-type a-BPDA imide oligomers (TriA-PI) with excellent processability. The resulting crosslinked PIs had high temperature resistance and greater than 20% ε_b after curing at 370 °C for 1 h.

Meanwhile, amorphous PIs derived from nonplanar and asymmetrical diamines have also been reported. Yang *et al.*^{18,19} reported PIs derived from PMDA and 3-phenyl-1,4-bis(4-aminophenoxy) benzene (p-TPEQ) that showed a higher T_g than bis(4-aminophenoxy)-benzene-based PI ($T_g = 272$ °C) at 286 °C. These results show that the pendant phenyl group of p-TPEQ restricts the free rotation of the ether linkage and produces a higher T_g because of the expansion of a free rotational unit in the PI chain. Morikawa *et al.*^{20–22} also reported the preparation and thermal properties of aromatic PIs derived from a

series of phenyl-group-substituted 4,4'-ODA derivatives. Particularly, a bis(4-amino-2-biphenyl)ether-based PMDA PI showed considerable improvements in solubility in polar aprotic solvents and a higher T_g at 303 °C than the above-described p-TPEQ-based PIs.

We previously described the dynamic tensile properties of novel PI derived from PMDA and 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA) as a diamine (Figure 1).²³ p-ODA, based on the 4,4'-ODA structure, has not only the simplest asymmetric, nonplanar and aromatic diamine structure but also the free rotational restriction of an ether linkage that exhibits a higher T_g than p-TPEQ-PIs. PI(PMDA/p-ODA) film exhibited a high T_g at 325 °C, good chemical stability, excellent mechanical properties and the formation of amorphous structures. The pendant phenyl group of p-ODA was markedly effective in causing typical PMDA-based aromatic PIs to form amorphous structures, as shown in Table 1.

In this work, based on the results presented above, we prepared phenylethynyl-terminated, addition-type PIs derived from PMDA and p-ODA (Figure 2). The PEPA-terminated PMDA/p-ODA aromatic imide oligomers ($n = 4$) were found to convert to the chain-extended polymers with excellent thermal stabilities ($T_g > 350$ °C) and mechanical properties (elongation-at-break, $\varepsilon_b > 14\%$) upon curing at 370 °C.

EXPERIMENTAL PROCEDURE

Materials

PMDA and 9,9-bis(4-aminophenoxy)fluorene (BAFL) were purchased from Tokyo Kasei Kogyo. *N*-Methyl-2-pyrrolidone (NMP) was purchased from Kanto Kagaku (Tokyo, Japan). PEPA was purchased from Manac (Tokyo, Japan). p-ODA was kindly supplied by Wakayama Seika Kogyo (Wakayama, Japan). The melting point of p-ODA was 116 °C. These materials were used as received.

Measurements

Differential scanning calorimetry (DSC) was performed using a thermal analyzer (DSC-2010; TA instruments, Newcastle, DE, USA) with the sample sealed in an aluminum pan. Glass transition temperatures (T_g) were determined with DSC at a heating rate of 20 °C min⁻¹ in a nitrogen atmosphere. DMA was performed on thin film specimens (23.7 mm long, 5 mm wide, 0.05–0.15 mm thick) on a rheometric solids analyzer (RSA II; Rheometrics, Tokyo, Japan) at a heating rate of 5 °C min⁻¹ and load frequency of 1 Hz in air. Melt viscosity measurements were performed with a dynamic rheometer (AR-2000; TA Instruments) at a heating rate of 5 °C min⁻¹. Compact resin disks with a 25-mm diameter and almost 2 mm thickness were prepared by press molding the powder-like imide oligomers at room temperature. High-resolution solution nuclear magnetic resonance (NMR) spectra were acquired using an NMR spectrometer (ASX-400; Bruker Analytik GmbH, Tokyo, Japan). Intrinsic viscosity measurements were performed in NMP at 25 °C using an Ubbelohde viscometer.

Figure 1 Structure of PI(PMDA/p-ODA). PI(PMDA/p-ODA) has a PMDA/4,4'-ODA backbone structure. p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PMDA, pyromellitic dianhydride; PI, polyimide.

Table 1 Thermal and mechanical properties of PI(PMDA/p-ODA) and PI(PMDA/4,4'-ODA) films

	$(\eta)_{NMP, 30^\circ C} (dl g^{-1})^a$	T_g (°C)		T_{d5} (°C) ^b	E_{ave} (GPa) ^c	σ_{brave} (MPa) ^d	$\varepsilon_{b,ave}$ (%) ^e
		DSC	DMA				
PI(PMDA/p-ODA)	2.0	333	325	549	3.3	158	38.5
PI(PMDA/4,4'-ODA)	3.5	— ^f	360 ^g	571	3.2	279	68.6

Abbreviations: DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; NMP, *N*-methyl-2-pyrrolidone; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PI, polyimide; PMDA, pyromellitic dianhydride.

^aInherent viscosity measured in NMP at 30 °C.

^b5% of weight loss measured in N₂.

^cAverage values of modulus.

^dAverage values of tensile strength.

^eAverage values of elongation at break.

^fNot detected obviously.

^gDetermined by the intersection of two tangent of storage modulus curve.

Figure 2 Structure of a phenylethynyl-terminated and addition-type imide oligomer ($n=4$) derived from pyromellitic dianhydride and 2-phenyl-4,4'-diaminodiphenyl ether. The imide oligomer has a Kapton-type backbone structure.

Preparation of asymmetric PIs derived from PMDA/p-ODA

PMDA/p-ODA and PMDA/4,4'-ODA PIs were prepared using a conventional two-step procedure through poly(amic acid)s with the corresponding diamine and dianhydride, as described in a previous report.²³

Preparation of PMDA/p-ODA/PEPA and PMDA/p-ODA;BAFL/PEPA imide oligomers

PEPA-terminated imide oligomers were synthesized using the following process (Supplementary Figures S1, S2 and S3).²³

A total of 5.0 mmol of p-ODA and NMP was added to a dried 100 ml, three-necked, round-bottom flask equipped with a nitrogen inlet and magnetic stirrer. After the diamine had dissolved completely, 4.0 mmol of PMDA was added and the reaction mixture was stirred for almost 2 h at room temperature in a nitrogen atmosphere. After the complete dissolution of PMDA, 2.0 mmol of PEPA was added with additional NMP to achieve the concentration of total solids of 33 wt% (w/w). The solution was stirred for another 6 h at room temperature.

After attaching a reflux condenser to the flask, the amide-acid oligomers in NMP solutions were imidized at 195 °C in an oil bath for 5 h. After the flask was cooled to room temperature, the resulting solution was completely clear with no precipitates. The solution was poured into water to reprecipitate the imidized oligomer. The precipitate was filtrated, washed with methanol, and dried at 220–260 °C in a vacuum oven for up to 4 h.

(PMDA/p-ODA/PEPA) = (4/5/2) imide oligomer (Supplementary Figure S4).

IR(KBr pellet): ν = 2211 (s), 1777 (s), 1726 (s), 1502 (s), 1483 (s), 1375 (s), 1232 (d), 1167 (s), 1113 (d), 820 (m), 756 (m), 724 cm⁻¹ (m).

¹H NMR(DMSO-*d*₆): δ (p.p.m.) 8.39 (t, 2H), 8.12–7.99 (m), 7.73–7.18 (m).

(PMDA/p-ODA; BAFL/PEPA) imide oligomers (Supplementary Figure S5).

IR(KBr pellet): ν = 2210 (s), 1777 (s), 1726 (s), 1502 (s), 1483 (s), 1376 (s), 1233 (d), 1167 (s), 1105 (d), 820 (m), 758 (m), 726 cm⁻¹ (m).

¹H NMR(DMSO-*d*₆): δ (p.p.m.) 8.39 (t, 2H), 8.12–8.01 (m), 7.73–7.21 (m).

Preparation of cured resins

The imide oligomers obtained were molded using a 6.0 cm × 6.0 cm × 0.05 mm PI film frame on a 20 cm × 20 cm stainless steel plate with UPILEX-S separator films under 1.4 MPa by heating initially to 310 °C for 10 min and subsequently to 370 °C for 1 h. Dark red film-like specimens of 6 cm × 6 cm × 0.05 to 0.10 mm were obtained.

RESULTS

Thermal and rheological properties of PMDA/p-ODA PIs

Figure 3 shows the temperature dependence of E' curves of PI(PMDA/p-ODA) and PI(PMDA/4,4'-ODA) films observed by DMA measurement in air. The PI(PMDA/4,4'-ODA) film showed a significant annealing effect caused by molecular ordering.^{24,25} In

Figure 3 Dynamic mechanical analysis (DMA) curves of PI(PMDA/4,4'-ODA) and PI(PMDA/p-ODA) films. A remarkably large drop in E' observed in DMA data of PI(PMDA/p-ODA). p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PMDA, pyromellitic dianhydride; PI, polyimide.

contrast, PI(PMDA/p-ODA) clearly showed not only a high T_g at 325 °C but also a remarkably large drop in E' from 10^9 to 10^7 Pa (rubbery plateau region) above T_g . These dynamic tensile behaviors of PI(PMDA/p-ODA) arose because the pendant phenyl group of p-ODA restricted the conformational change of PMDA/4,4'-ODA backbone structure, because of its rotational inflexibility of ether linkage and the intramolecular/intermolecular interactions of PI chains and because of its nonplanar and bulky steric hindrance. An increase in E' was observed at temperatures close to 420 °C because of thermo-oxidative crosslinking caused by the measurement being performed in air. Wide-angle X-ray diffraction patterns of PI(PMDA/p-ODA) showed only a broadened peak without dependence on annealing temperature, suggesting the formation of an amorphous structure.²³

The thermal and mechanical properties of PI(PMDA/p-ODA) determined by DSC and tensile measurements are presented in Table 1. PI(PMDA/p-ODA) showed high thermal stability up to 500 °C in nitrogen atmosphere and a high temperature of T_d5 (549 °C) from thermogravimetric analysis. Moreover, PI(PMDA/p-ODA) was also found to be very mechanically tough, with elongation-

Table 2 Thermal and mechanical properties of (PMDA/p-ODA/PEPA) imide oligomer ($n=4$) and its cured resin

Diamine	$(\eta)_{NMP, 30^\circ C} (dl g^{-1})^a$	Solubility (wt%(w/w)) ^b	Min. melt viscosity ($Pa s^{-1}$) ^c	Cured resin ^d			
				T_g ($^\circ C$)		T_{d5} ($^\circ C$) ^d	$\varepsilon_{b,ave}$ (%) ^e
				DSC	DMA		
p-ODA	0.14	>33 ^f	208	354	346 ^g	527	17.4

Abbreviations: DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; NMP, *N*-methyl-2-pyrrolidone; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PEPA, 4-phenylethynyl phthalic anhydride; PI, polyimide; PMDA, pyromellitic dianhydride.

^aInherent viscosity measured in NMP at 30 $^\circ C$.

^bSolubility in NMP.

^cDetermined by rheometer.

^dCured at 370 $^\circ C$ for 1 h.

^e5% of weight loss measured in air; average values of elongation at break.

^fGelation after 1 day.

^gDetermined by the intersection of two tangent of storage modulus curve.

Figure 4 Differential scanning calorimetry curves of the 4-phenylethynyl phthalic anhydride-terminated PMDA/p-ODA imide oligomer (first run) and its cured resin (second run). The PMDA/p-ODA imide oligomer and its cured resin showed T_g at 213 $^\circ C$ and at 356 $^\circ C$, respectively. p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PMDA, pyromellitic dianhydride.

Figure 5 Dynamic rheological properties of the PMDA/p-ODA/PEPA ($n=4$) imide oligomer. The imide oligomer showed very low minimum melt viscosity ($200 Pa s^{-1}$). p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PEPA, 4-phenylethynyl phthalic anhydride; PMDA, pyromellitic dianhydride.

at-break of almost 40%. These properties were similar to those of PI(PMDA/4,4'-ODA).

Physical properties of phenylethynyl-terminated PMDA/p-ODA imide oligomers

PMDA-based imide oligomers ($n=4$) derived from 4,4'-ODA or p-ODA were obtained from the imidization of the solution of corresponding amide-acid oligomers at 195 $^\circ C$ for 5 h. The PMDA/4,4'-ODA/PEPA imide oligomer was insoluble in NMP and was not processable to cured resin because its T_g was higher than 370 $^\circ C$ (Table 2 and Supplementary Figure S6). However, the PMDA/p-ODA/PEPA imide oligomer ($n=4$) was completely soluble in NMP solution at high concentrations, even at room temperature (>30 wt%).

Figure 4 shows the DSC curve of the PMDA/p-ODA imide oligomer (first run) and its cured resin (second run). The DSC curve of the uncured PMDA/p-ODA imide oligomer showed an endothermic shift at its T_g of approximately 213 $^\circ C$. A large peak due to exothermic chain extension by the curing reaction of the endcapped phenylethynyl groups is seen at temperatures between 320 and 460 $^\circ C$. The subsequent run showed only a baseline deflection at

approximately 356 $^\circ C$, indicating that the imide oligomer had fully converted into the cured resin with an extremely high T_g .

The dynamic rheological property of the PMDA/p-ODA/PEPA imide oligomer is shown in Figure 5. Surprisingly, the imide oligomer exhibited a low dynamic melt viscosity of only $200 Pa s^{-1}$ at approximately 340 $^\circ C$, signifying a considerable improvement in the processability of PMDA-based PI resins for molding fiber-reinforced heat-resistant composites.

Thermal and mechanical properties of cured resins

Thermal and mechanical properties of the cured resin are presented in Table 2. The T_g values observed by DSC (354 $^\circ C$) and DMA (346 $^\circ C$) were found to be extremely high. As shown in Figure 6, E' of the cured resin also showed a remarkably large drop above T_g , similar to PI(PMDA/p-ODA). An increase in E' was also observed at temperatures close to 420 $^\circ C$ because of thermo-oxidative crosslinking that occurred during measurements in air. The ε_b of the cured resin was found to be exceedingly high (>14%), indicating that the thermal reaction mechanism of the PEPA was mainly chain extension without further cyclization or crosslinking, as also reported by McGrath *et al.*^{8–10}

Figure 6 Dynamic mechanical analysis curve of the cured resin. E' of the cured resin showed a remarkably large drop above T_g (>345 °C).

Figure 7 Three possible types of repeated units in a (PMDA/p-ODA) polymer chain. Three possible types ((a) head-to-head, (b) head-to-tail and (c) tail-to-tail) of repeated units exist because of the asymmetric structure of p-ODA. p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PMDA, pyromellitic dianhydride.

Incorporation of BAFL diamine monomer into PMDA/p-ODA/PEPA imide oligomers

After preparing a highly concentrated NMP solution of the PMDA/p-ODA/PEPA imide oligomer (33 wt%, $n=4$) at 150 °C, the solution

Figure 8 Chemical structure of 9,9-bis(4-aminophenoxy)fluorene (BAFL) diamine. BAFL has a bulky fluorenyl group that improves the solubility of the imide oligomer. The quaternary carbon atom of BAFL has free rotational inflexibility.

Figure 9 Dynamic mechanical analysis curves of PI(PMDA/p-ODA;BAFL) as the concentration dependency of the BAFL ratio for all diamines. A decrease in the drops of E' to the rubbery plateau region above T_g was observed with an increase in the BAFL concentration. BAFL, 9,9-bis(4-aminophenoxy)fluorene; PMDA, pyromellitic dianhydride; PI, polyimide; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether.

was allowed to gel during storage for 1 day at room temperature. When the gel was later heated to 150 °C for 1 h, it gradually changed to a solution without precipitation. This sol–gel reaction could be repeated reversibly. Consequently, three types of repeating units (head-to-tail (a), head-to-head (b) and tail-to-tail (c)) could exist in a PMDA/p-ODA oligomer chain (Figure 7). The sol–gel behavior described above is conceivably attributed to the intermolecular interaction of the 18 Å long planar and rigid phenyl–pyromellitimide–phenyl structures of the tail-to-tail units (c) in oligomer chains.

In general, more than 30 wt% of the matrix resin is required to exist in solution form without gel and precipitation to enable the molding of the carbon-fiber reinforced composites via the imide oligomer prepreps (manufactured by dipping carbon fibers in a highly concentrated imide oligomer solution). The above phenomenon strongly suggests that the PMDA/p-ODA imide oligomer is necessary to act as a third component for increasing its solubility.

The bulky substituent of the polymer side chain improves solubility by increasing solvation. We selected BAFL with a bulky side fluorenyl group as a candidate for copolymerizing the diamine monomers to PMDA/p-ODA imide oligomers (Figure 8).²⁶

Table 3 Solubility and minimum melt viscosities of (PMDA/p-ODA;BAFL/PEPA) imide oligomers

Mol. ratio of p-ODA/BAFL	Calculated Number-average molecular weight ($M_n \times 10^{-3}$)	$(\eta)_{NMP, 25^\circ C} (dl g^{-1})^a$	Solubility (wt%(w/w)) ^b	Min. melt viscosity (Pas ⁻¹) ^c
95/5	2.6	0.14	> 33 ^d	226
90/10	2.6	0.14	> 33 ^d	154
75/25	2.6	0.14	> 33 ^d	1323
50/50	2.7	0.14	> 33 ^e	731
25/75	2.8	— ^f	— ^f	— ^g

Abbreviations: BAFL, 9,9-bis(4-aminophenyl)fluorene; NMP, *N*-methyl-2-pyrrolidone; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PEPA, 4-phenylethynyl phthalic anhydride; PI, polyimide; PMDA, pyromellitic dianhydride.

^aInherent viscosity measured in NMP at 30 °C.

^bSolubility in NMP.

^cDetermined by rheometer.

^dSolution for a few months.

^eGelation after 1 day.

^fInsoluble.

^gInfusible.

Table 4 Thermal and mechanical properties of (PMDA/p-ODA;BAFL/PEPA) cured resins

Mol. ratio of p-ODA/BAFL	T_g (°C)		T_{d5} (°C) ^a	$\epsilon_{b,ave}$ (%) ^b
	DSC	DMA		
95/5	353	350 ^c	538	11.7
90/10	372	356 ^c	538	11.3
75/25	392	369 ^c	533	7.4
50/50	— ^d	— ^e	532	4.7

Abbreviations: BAFL, 9,9-bis(4-aminophenyl)fluorene; DMA, dynamic mechanical analysis; DSC, differential scanning calorimetry; p-ODA, 2-phenyl-4,4'-diaminodiphenyl ether; PEPA, 4-phenylethynyl phthalic anhydride; PI, polyimide; PMDA, pyromellitic dianhydride.

^a5% of weight loss measured in air.

^bAverage values of elongation at break.

^cDetermined by the intersection of two tangent of storage modulus curve.

^dNot detected obviously.

^eBrittle.

Figure 9 shows DMA curves of PI(PMDA/p-ODA;BAFL) as a function of the BAFL concentration for all diamines. A decrease in E' to the rubbery plateau region above T_g was observed with an increase in the BAFL concentration. The results show that the molecular mobility of PI(PMDA/p-ODA) chains was reduced with an increase in the rigid zigzag structures of phenyl-pyromellitimide-phenyl (PMDA-BAFL-PMDA) units. This reduction in mobility was due to the restriction in the free rotation of the quaternary carbon atoms by steric hindrance of hydrogen atoms at 2- and 2'-positions of the bis(4-aminophenyl) group in BAFL. However, at concentrations of up to 25 mol-% of BAFL, large drops in E' remain observable in the DMA curves. The data strongly suggest that PMDA/p-ODA imide oligomers with an optimal ratio of BAFL (<25 mol-%) showed sufficient processability in the cured resins with high T_g .

Table 3 shows the solubility and minimum melt viscosities of phenylethynyl-terminated PMDA/p-ODA;BAFL imide oligomers with a different copolymerized ratio of p-ODA/BAFL (Supplementary Figure S7). The addition of a small amount of BAFL (5 or 10 mol-% for the total diamine) was sufficient to allow the imide oligomers to be stored as a clear solution for several months without sacrificing their melt viscosity. Table 4 presents the thermal and mechanical properties of their cured resins. These T_g values were found to increase with increasing BAFL at temperatures close to 350 °C. In contrast, a decrease in the ϵ_b values of the cured resins was observed with increasing BAFL. The results show that the molecular mobility

and flexibility derived from ether linkage of p-ODA in polymer chains decreased concomitantly with increasing number of rigid units of PMDA-BAFL-PMDA. Particularly, the addition of only 5–10 mol-% of BAFL allowed the imide oligomers to convert into cured resins with very high T_g (>350 °C) and good ϵ_b (>13%). All cured resins also showed high thermal-oxidation stability (Supplementary Figure S8).

On the basis of these results, the phenylethynyl-terminated PMDA/p-ODA;BAFL imide oligomers were found to have high solubilities (>33 wt%) and storage stabilities (<1500 Pa s⁻¹) over the content range of <25 wt% of BAFL. They exhibited very low melt viscosities and converted to cured resins with both high T_g (>350 °C) and good mechanical properties (ϵ_{bs} > 13%).

Detailed studies of the thermal and mechanical properties of phenylethynyl-terminated imide oligomers, derived from PMDA and p-ODA with mainly 10% of BAFL, and the processability for fiber-reinforced composites are in progress.^{27–29} We believe that these PMDA/p-ODA-type imide oligomers will greatly enhance the possibilities for developing new high-quality and excellent heat-resistant composite materials with good processability.

CONCLUSIONS

A novel phenylethynyl-terminated, addition-type imide oligomer ($n=4$) derived from PMDA and p-ODA was found to have high solubility and good processability. The imide oligomer was converted to a cured resin with a high T_g and excellent mechanical properties at 370 °C. The incorporation of BAFL into (PMDA/p-ODA/PEPA) was found to increase the solubility of the imide oligomer without sacrificing its melt viscosity. Particularly, even the addition of a small amount of BAFL resulted in cured resins with higher T_g (>350 °C) and good ϵ_{bs} (>13%).

We believe that these excellent properties of PMDA/p-ODA-based, addition-type aromatic PIs are promising for applications in highly heat-resistant composites.

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